DEVELOPMENT AND EVALUATION OF CATALYSTS FOR PRODUCTION OF LIQUID FUELS FROM LOW GRADE HYDROCARBON SOURCES

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Final Report

by

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SUMMARY

A test program was carried out with selected commercial catalysts and reduced molybdenum catalyst on hydrogenation of feedstocks consisting of refinery pitch, anthracene oil and three solvent refined coals.

The solvent refined coals were prepared by hydrogenation of coal with tetralin in a 2 L autoclave; crude liquids were extracted with tetrahydrofuran and materials boiling above 208°C were used for hydrotreating experiments. Hydrotreating tests were carried out with the different catalysts using a tubing bomb apparatus to determine yields of selected products.

The product distributions varied, due to the initial nature of the feedstock, but differences were observed between tests without catalyst and with the different catalysts. The product distributions were more favourable for tests with catalysts and the commercial catalysts were slightly more efficient than reduced molybdenum. The hydrogen consumptions were also higher for experiments using the commercial catalyst.

Recycling the catalysts with a solvent refined coal resulted in similar product distributions, but the oil derived from the commercial catalyst was superior in quality.

Analyses of carbon disulphide extracts obtained from catalytic hydrotreatment of the feedstocks indicated increases in hydrogen content, decreases in heteroatom content and an improvement in boiling range for the products compared to the initial feedstocks. The performances of the catalysts were similar, and differences in product composition were primarily dependent on the initial feedstock.

Overall, test results on solvent refined coal feedstocks indicate high production of insoluble residue, low conversion to hexane soluble oils and low hydrogen consumptions. These results suggest that hydrotreatment of undiluted heavy products of coal conversion is not a viable approach.

For the particular case of Greenhills solvent refined coal, sulphided unsupported molybdenum catalysts resulted in less insoluble residue than commerical CoMo and NiMo formulations. Further testwork would be required to determine whether optimization of conditions with commercial catalysts can achieve comparably low residues.

INTRODUCTION

BACKGROUND

Preliminary studies have shown that high yields of crude coal derived liquids can be obtained from direct liquefaction of selected Canadian coals. However, the initially produced "liquids" contain high proportions of asphaltene and preasphaltene materials, so substantial upgrading would be required to produce transport type fuels required by the Canadian market.

In heavy oil hydrodesulphurization plants, extensive use is made of commercially available catalysts which consist of sulphided cobalt or nickel and molybdenum supported on alumina. Results of process development studies by Dow Chemical Company (1) and laboratory research at the University of Ottawa (2) indicated that dispersed forms of molybdic oxide and silica - supported molybdenum metal were also active catalysts for upgrading of heavy hydrocarbon liquids.

Thus, for a particular feedstock (e.g. coal derived liquid or heavy oil), the performances of commercial formulations (eg. cobalt or nickel/molybdenum on alumina) represent a baseline for evaluation of other systems which may offer technical and/or economic advantages.

The Dow Chemical Co. process studies involved dispersion of chemically refined molybdic oxide in raw coal before initial liquefaction, with some internal recycle of fine ($\leq$ 2 micron diameter) molybdenum

catalyst and no recovery of molybdenum from the residue. Electron micro-probe examinations of solids recovered from the liquefaction products indicated that the molybdenum was normally present as molybdenum disulphide. The catalyst activation was presumed to include the following transformations (1):

$$\text{Ammonium heptamolybdate} \xrightarrow{\Delta} MoO_3 + NH_3 + H_2O$$

$$MoO_3 + H_2 + 2H_2S \rightarrow MoS_2 + 3H_2O$$

The University of Ottawa bench scale study results indicated that molybdenum (deposited on a silica substrate by sorption and decomposition of molybdenum hexacarbonyl (2)) was chemically active at low temperature in the desulphurization of benzothiophene. It is reasonable to expect that molybdenum sulphide thus formed would be at least as catalytically active as MoS_2 formed by the interaction of ammonium molybdate with hydrogen sulphide under coal liquefaction conditions. (Note that whatever the chemical form of molybdenum on silica initially, molybdenum sulphide surfaces will be formed from hydrogen sulphide produced by reduction of benzothiophene.)

Molybdenum metal powder is conveniently prepared by atmospheric pressure carbothermic reduction of molybdic oxide. Molybdic oxide is currently produced in Canada by Placer Development Ltd.; potential sources of reducing carbon are fluid and delayed coking operations in the petroleum industry.

Given the known catalytic activity of molybdenum sulphide and the chemical activity of supported molybdenum metal both initially and after sulphide exposure, it would be reasonable to expect that molybdenum metal (or partially reduced oxide) powder would be chemically and catalytically active in the hydrogenation/ desulphurization of crude hydrocarbons.

If this assumption is correct, there are other potential advantages in using reduced molybdenum catalyst for crude liquid upgrading which include:

- carbothermal metallic catalyst would obviate the requirement for hydrogen reduction of the molybdic oxide during liquefaction or upgrading.
- recovery/reactivation by simple low temperature oxidation of solid residue (coke or filter cake) without chemical refining and refabrication of the supported catalyst.
- chemical desulphurization activity of the catalyst as added.

With reference to upgrading of heavy crude oil or refinery residue, the metals normally present (iron, vanadium, nickel) will deposit on hydrotreating catalyst surfaces. Recovery and reactivation of the catalyst used for upgrading these materials could include steps for partial or complete recovery of nickel and vanadium.

The present study involved tests on commercial catalysts to establish baseline data on the upgrading potential for crude hydrocarbons. Tests with reduced molybdenum were undertaken to determine whether catalysts of this type offer technical and/or economic advantages over currently used systems.

OBJECTIVES

Objectives of this study were:

- to determine the performance of commercial cobalt-molybdenum and nickel-molybdenum based catalysts on refinery pitch and crude liquid derived from Canadian coals.

- to prepare reduced molybdenum powder catalysts by carbothermic reduction of commercial molybdenum oxide.

- to determine performance of the prepared catalysts on the crude liquids tested previously.

- to evaluate and compare technical and economic aspects of the different catalyst systems.

METHODS AND MATERIALS

HYDROCARBON PREPARATION AND UPGRADING PROCEDURE

Materials used in this study were a pitch (vacuum residue) from the IOCO, B.C. refinery, an anthracene oil supplied by the Nova Scotia Research Foundation (origin not known) and coal derived liquids prepared from the B.C. Coal Ltd. Greenhills Mine (medium volatile western metallurgical coal), Devco 26 Harbour Seam (eastern high volatile metallurgical coal) and Hat Creek (western sub-bituminous coal).

The coal derived liquids were prepared by hydrogenating the coals in a two litre Autoclave Engineers Ltd. autoclave using tetralin solvent and hydrogen at 420°C for one hour. Initial cold hydrogen pressure was 6.8 MPa; maximum pressure at operating temperature was ~10.5 MPa. Solvent to coal ratio was 3:1. The crude liquids were separated from solid residue after liquefaction by extraction with tetrahydrofuran (THF). The extract was distilled to remove the THF and hydrocarbon products with atmospheric boiling points below 208°C. The residue boiling above 208°C for each coal was then stored under nitrogen at -10°C for use in the catalytic upgrading studies.

Catalytic upgrading studies were carried out in a "tubing bomb" batch process shown in Figure 1. The tubing bomb consists of a small piece of capped stainless steel pipe, fastened to a shaker. Each bomb was loaded with 20 g of material and the required weight of catalyst. The

bomb was then sealed, flushed with hydrogen several times, and pressurized to an initial cold pressure of 6.8 MPa (1000 psig). The bomb was then immersed in a preheated fluidized sand bed. Experimental heat-up times from ambient to test temperature were in the range of 4 to 5 minutes. The bomb was held at reaction temperature for the required time while the temperature and pressure were continuously monitored. During the heat-up and reaction periods, the bomb and its contents were vigorously agitated by the shaker. At the end of the experiment, the bomb was taken out of the bed and rapidly cooled with a jet of high pressure moist air. The cooled bomb was depressurized and a gas sample was taken for analysis by chromatography. The product was quantitatively washed out of the bomb and analyzed to determine product slate and total conversion.

HYDROCARBON SEPARATION AND CHARACTERIZATION

In order to determine the product slate the hydrotreated material was washed out of the bomb with toluene, filtered through a tared soxhlet thimble and extracted with toluene until clear. The toluene extracts were combined and the toluene was evaporated to a constant weight using a rotary evaporator. Hexane was added to the remaining liquid to precipitate asphaltene. Residue remaining after the soxhlet extraction with toluene was extracted with THF to determine the preasphaltene and THF insoluble residue.

To overcome problems of moisture and catalyst contamination in some of the experiments, the products needed for comparison with the original hydrocarbons were washed from the bombs with carbon disulphide, a polav compound having good solvency for the liquids. These were then filtered through a tared soxhlet thimble and extracted with carbon disulphide in the soxhlet apparatus until clear. The carbon disulphide was evaporated and the remaining product was used to carry out the required characterization tests.

The samples of refinery pitch, anthracene oil and the coal derived liquids, together with selected products from catalytic hydrotreating, were characterized by:

- proximate and ultimate analyses
- ^{1}H NMR spectra recorded at 250 MHz by the University of Victoria, Department of Chemistry
- thermogravimentric analyses using a Dupont 1090 Thermal Analyzer
- solvent extraction using hexane, toluene, and THF or pyridine which gave the oil, asphaltene and preasphaltene content respectively.
- chromatographic analyses of gas products and known volumes of the bombs and gas lines were used to calculate the gas make and hydrogen consumption as wt.% of daf starting material.

CATALYST PREPARATION

Commercial catalysts used in this study were Cyanamid HDS 1442A (CoMo) and HDS 3A (NiMo), both having alumina support. Pellets were crushed to -70 mesh. Chemical compositions are shown in Table 1.

Cyanamid catalysts were presulphided by reacting with creosote oil, sulphur and hydrogen in the "tubing bomb" at an initial cold pressure of 6.8 MPa. The creosote oil to catalyst ratio was 3:1 and a 50% stoichiometric excess of sulphur was used. Mixtures were heated for 30 minutes at 300°C with an initial hydrogen pressure of 5.4 MPa. Products were washed free of the liquid with THF, vacuum dried and stored under nitrogen.

The reduced molybdenum catalyst was prepared by reduction of molybdenum (VI) oxide with carbon in a ratio of 1:8 by weight at 650°C in a tube furnace under flowing nitrogen. Time at temperature was 30 minutes.

RESULTS AND DISCUSSION

CHARACTERIZATION OF THE INITIAL FEEDSTOCKS

Proximate analyses of initial feedstocks (Table 2) indicated that volatile matter contents of the refinery pitch and anthracene oil were similar and were much higher than corresponding values for the solvent refined coals. The volatile matter contents of the solvent refined coals increased with decreasing rank of the original coals. Moisture and ash levels were low or nil for the initial feedstocks.

Ultimate analyses (Table 2) indicated that hydrogen and sulphur contents of the refinery pitch were much higher than the other materials. The nitrogen and oxygen values for the solvent refined coals were higher than those for the refinery pitch and anthracene oil.

^{1}H NMR spectroscopic data (Table 3) indicated that the hydrogen content of the refinery pitch was mainly aliphatic, the balance being olefinic rather than aromatic in nature. Aromatic to aliphatic hydrogen ratios for the coal liquids decreased with decreasing rank of the original coals.

Results of thermogravimetric analyses (Table 4) indicate that the anthracene oil and refinery pitch are largely distillable at temperature $\leq$ 500°C. (Note that TGA distillation data are used throughout this report for uniformity since the amount of material produced in a tubing bomb test is insufficient for a full distillation

test. Simulated distillation by gas chromatography gives - at best - unreliable values for +525°C residue. TGA data correlate reasonably well with actual distillation data and give reliable data on non-distillable residues.

The solvent refined coals contained large proportions of non-distillable material. The decrease in +500°C residue for the coal derived liquids reflected the trend shown by the volatile matter (Table 2) and the decrease in aromaticity of the product shown by the data from the ^{1}H NMR spectra (Table 3).

Sequential extraction of the initial feedstocks also showed very different product distributions. The refinery pitch and anthracene oil consisted mainly of oil (i.e. hexane soluble material) with little or no asphaltene, preasphaltene, or pyridine insoluble residue. The coal derived liquids consisted mainly of asphaltenes and preasphaltenes (Table 5). The presence of pyridine insoluble residues in the solvent refined coal liquids was surprising considering that all the material was originally soluble in THF. These residues may have been derived from polymerization and/or oxidation reactions which could have occured during the removal of the low boiling material, THF and tetralin at 208°C.

PRESULPHIDING CONDITIONS FOR COMMERCIAL CATALYSTS

Information supplied by Cyanamid indicated that the presulphiding reaction should take place at 300°C as temperature in excess of this

value could cause coking of the catalyst. Samples of the catalysts prepared by presulphiding at 300°C and 400°C temperatures (the later to model sulphiding under anticipated reactor conditions) were reacted with anthracene oil; results are presented in Table 6.

These data indicate better performance by the catalyst presulphided at 300°C, so this temperature in conjunction with the conditions mentioned previously were used for subsequent presulphiding of the Cyanamid HDS 1442A (CoMo) and HDS 3A (NiMo) catalysts.

EFFECT OF SULPHIDED HDS 1442A (CoMo) CATALYST ON THE INITIAL FEEDSTOCKS

Presulphided HDS 1442A (CoMo) catalyst was tested with refinery pitch, anthracene oil and the coal derived liquids. Catalyst loading was equivalent to 10 wt.% of the hydrocarbon material. The effects of temperature and time were investigated and the test sequence in each case involved a temperature series of 375, 400 and 425°C and a time series of 15, 30 and 60 minutes.

Refinery Pitch

Product distribution data for refinery pitch with catalyst at different temperatures, and for a reaction time of 30 minutes (Table 7), indicated little change compared with the results for the solvent extraction of untreated pitch. However, the presence of catalyst was beneficial when compared to the experiment carried out at equivalent conditions without catalyst. The presence of catalyst seemed to

prevent the degradation of oil to asphaltene.

The highest oil yield was obtained at a temperature of 425°C and a time study was therefore carried out at this temperature (Table 7). A maximum oil yield was obtained at a temperature of 425°C and a time of 30 minutes. Although this yield was not as high as that obtained by the solvent extraction of the untreated pitch, these conditions were adopted for further catalyst testing with the refinery pitch.

The hydrogen consumption increased with the addition of catalyst, and with the increase in reaction temperature and time, probably due to heteroatom removal.

The boiling range of the oil fraction (hexane soluble material) derived from the catalytic hydrogenation of refinery pitch was determined by thermogravimetric analyses (Table 8). The material boiling below 350°C increased with the increasing temperature and time up to 30 minutes. The major fraction of the oil produced in these experiments was in the 350-500°C boiling range.

The addition of sulphided HDS 1442A (CoMo) catalyst improved the boiling range of the oil (ibp - 350°C), but not the quantity compared to results for the solvent extraction of the initial feedstock (Table 7).

Anthracene Oil

Hydrogenation of anthracene oil with sulphided HDS 1442A (CoMo) catalyst resulted in a product distribution with a high hexane soluble oil content (Table 9). The addition of catalyst increased the oil yields while reducing the asphaltene, and THF insoluble residues compared to results obtained for the experiment without catalyst, and for the solvent extraction of the initial feedstock. However - apart from a small increase in the THF insoluble residues - these catalyst tests on anthracene oil, with variation in temperature and time, showed little change in product distribution.

As for the refinery pitch, hydrogen consumption increased with addition of catalyst and with the increase in reaction temperature and time. These values were higher than those obtained with refinery pitch, and - in addition to heteroatom removal - some of the hydrogen may have been used to saturate aromatic rings in the anthracene oil.

Thermogravimetric analyses (Table 10) of the hexane soluble oils produced in these experiments with catalyst showed that the material boiling below 350°C only varied slightly with temperature or time. However, there was an improvement compared to experiments without catalyst. Unlike the oil derived from refinery pitch, where the major fraction was in the 350-500°C boiling range, the hexane soluble oil derived from anthracene oil consisted mainly of the 200-350°C fraction.

Greenhills SRC

Test data presented in Table 11 show that product distribution improved with temperature and time when sulphided HDS 1442A (CoMo) catalyst was used in hydrotreating tests on Greenhills SRC. Unlike the catalytic hydrotreated products discussed previously, the major constituent obtained with the solvent refined coal was asphaltene rather than oil. The preasphaltenes and residues in these experiments were also much greater than those obtained from refinery pitch and anthracene oil.

It has been shown that solvent refined coal is susceptible to oxidation (3) and - although precautions were taken - some oxidation may have occurred during the preparation of the intial feedstock, resulting in the high THF insoluble residue. However, the preasphaltene content of this initial material is high (Table 5) and preasphaltenes have been shown to yield up to 80% char on pyrolysis in an inert atmosphere (4). This char formation occurs in the coal liquefaction temperature range and this may contribute to the high residue obtained during the processing of the Greenhills SRC without the diluting effect of material boiling below 208°C. Model compound studies have indicated char formation increased with phenol content, but no model compounds could be found that were as efficient in producing char as preasphaltenes (4).

The addition of catalyst, and the increase in temperature and time seemed to reduce this retrogressive reaction and increased the asphaltene content.

The hydrogen consumption increase with temperature and time and was much less than for anthracene oil. The heteroatom content of the Greenhills SRC was greater than that of the anthracene oil, except for sulphur, so a greater hydrogen consumption would be expected. However, preasphaltenes have been shown to produce less oil, form more char and consume less hydrogen than asphaltenes (4). The oil fraction has also been shown to consume more hydrogen than the preasphaltenes during liquefaction (3). Thus Greenhills SRC, which has a higher preasphaltene and lower oil content than coal derived anthracene oil, may consume less hydrogen in upgrading. The hydrogen consumption for the refinery pitch was similar to the Greenhills SRC, but this product is aliphatic (i.e. highly saturated compared to the aromatic anthracene oil).

The oil yields in these experiments were small so boiling ranges were not determined by thermogravimetric analyses.

Devco SRC

Test data presented in Table 12 show that major product obtained by the addition of sulphided HDS 1442A (CoMo) catalyst to Devco SRC was asphaltene. This component increased with the addition of catalyst and with the increase in temperature and time. The asphaltene yields

for the Devco samples were higher and the preasphaltenes and residues were lower than the corresponding yields for the Greenhills SRC. The more favourable results for the Devco SRC were probably due to the higher volatile matter and greater hydrogen consumption. The heteroatom content was equivalent to the Greenhills SRC so the slight increase in hydrogen consumption was probably utilized in asphaltene formation from preasphaltene.

Due to insufficient oil samples, the boiling ranges were not determined.

Hat Creek SRC

The solvent refined coal derived from Hat Creek, a subituminous coal, was different in character when compared with the other two coal derived liquids. Sequential extraction of the untreated Hat Creek SRC resulted in a product with a high asphaltene content, whereas preasphaltene was the predominant component in the other two SRC feedstocks.

As indicated by the data of Table 13, quality of the product obtained by hydrogenating Hat Creek SRC improved with the addition of sulphided HDS 1442A (CoMo) catalyst and with the increase in reaction temperature and time. The oil yields increased under these conditions, and were much greater than the oil yields obtained from the other two coal derived feedstocks.

The major hydrogenation product was asphaltene in all tests. However, in contrast to the other SRC feedstocks treated, the proportion of asphaltene remained constant or decreased slightly with increasing time and temperature. This was probably due to the reduction of the high oxygen content of the Hat Creek SRC, which is usually concentrated in the asphaltene component of the final product (3).

Preasphaltenes and THF insoluble residues were small compared to the other two coal derived feedstocks. These low residues would seem to indicate that the preasphaltenes contain less of the precursors which are susceptible to oxidation and/or coking, than those derived from bituminous coal.

The hydrogen consumption was much greater for the Hat Creek SRC than for the bituminous coal SRCs, probably due to the higher initial oxygen content and the greater demand due to the (relatively) high asphaltene and oil yields.

The unaccounted for product and/or error was larger than usually observed (product total is usually within $\pm$ 4% of the total conversion value obtained via the THF insolubles) and these Hat Creek results were not normalized to 100%. This difference was mainly due to the formation of water (4%) which was determined by azeotropic distillation with xylene using the whole product from an experiment with Hat Creek and sulphided HDS 1442A (CoMo) catalyst.

CONDITIONS FOR COMPARISON TESTING NiMo AND REDUCED Mo CATALYSTS

TGA distillation data (Table 14) on the oil fraction of 425°C hydrogenated Hat Creek SRC indicate that both catalyst and increased time at temperature improved the yield of ibp-200°C and 200-350°C fractions. Conditions for further catalyst testing and performance evaluation were selected as a temperature of 425°C and a time of 30 minutes. However, because of the large oil yield and improvement in quality with time for Hat Creek SRC (Tables 13 and 14) a temperature of 425°C and a time of 60 minutes was also chosen for further selected catalyst testing on this material.

EFFECT OF SULPHIDED HDS 3A (NiMo) CATALYST ON THE INITIAL FEEDSTOCKS

The effects of adding sulphided HDS 3A (NiMo) catalyst to the feedstocks discussed proviously were studied at the comparison conditions of 425°C and 30 minutes. The catalyst loading was equivalent to 10 wt.% of the feedstock. Test data are presented in Table 15.

There was little change in the product distribution with NiMo catalyst, compared to the results obtained with the sulphided HDS 1442A (CoMo) catalyst. The hydrogen consumptions with NiMo were marginally higher, possibly due to (claimed (5)) greater heteroatom removal and saturation of aromatic rings by this catalyst.

The boiling ranges (Table 16) of oils obtained in these experiments indicated that they were of a heavier quality than those obtained by the addition of sulphided HDS 1442A (CoMo) catalyst to the feedstocks.

EFFECT OF REDUCED MOLYBDENUM CATALYST ON THE INITIAL FEEDSTOCKS

The reduced molybdenum catalyst was added to the initial feedstocks to give molybdenum concentrations equivalent to the molybdenum concentration in the HDS 1442A (CoMo) catalyst. Initially the reduced molybdenum catalyst was prepared in two different mesh sizes (-70 and -100 mesh) and tested with the feedstocks. The addition of sulphur (0.5 g) with the catalyst was found to be beneficial in some experiments but not in others. In the case of the Greenhills SRC, the effect of sulphur was unequivocally positive; in other tests, the differences were less clearly defined.

A reaction temperature of 425°C and a time of 30 minutes was used in these experiments; results obtained are shown in Table 17.

Refinery Pitch

The product distribution obtained by catalytic hydrogenation of refinery pitch with reduced molybdenum showed little variation with catalyst particle size or with the addition of sulphur.

The THF insoluble residues were greater and the oil yields were marginally lower than the results obtained with commercial catalyst. This lower efficiency was reflected in the lower hydrogen consumptions compared to those for the commercial catalysts (Tables 15 and 17). The product distributions were not as good as the results obtained by thermal hydrotreatment without catalyst.

The boiling range distribution of the oils obtained in these experiments with reduced molybdenum compared favourably with results for the commercial sulphided HDS 3A (NiMo) catalyst, but was not as good as for sulphided HDS 1442A (CoMo) catalyst or for the experiment without a catalyst. The differences are clearly distinguishable analytically, but not large in absolute terms.

Anthracene Oil

A more positive effect was obtained by adding reduced molybdenum to anthracene oil. The best results were obtained with the -100 mesh material and this result, apart from the higher THF insoluble residue, compared favourably with the results obtained with the commercial catalyst. The hydrogen consumptions were lower than those obtained with the commercial catalysts, probably due to lower heteroatom removal (Table 15 and 17) or possibly caused by lack of sulphur in conjunction with the sulphided commercial catalysts.

Conversions of anthracene oil under the uniform test conditions were as follows:

	Product Distribution (wt.% daf)		
	Oil	Asphaltene	Residue
Hydrotreated, no catalyst	88.1	10.5	1.4
Sulphided HDS 1442 A(CoMo)	97.7	1.3	0.8
Sulphided HDS 3A (NiMo)	96.0	0.8	3.1
Reduced Mo (-100 mesh)	95.2	0.7	4.0
Feedstock	89.8	5.8	4.4

The use of reduced molybdenum catalyst with anthracene oil produced equivalent oil, and asphaltene, compared to commercial catalyst hydrotreatment, but the toluene insoluble residue was the highest of the catalytic tests and only marginally less than the feedstock.

The boiling range distribution for the oils produced compared favourably with results obtained for sulphided HDS 3A (NiMo) catalyst and thermal hydrotreatment, but were not as good as those obtained with sulphide HDS 1442A (CoMo) catalyst (Tables 16 and 18).

	TGA Distillation (wt.%) of Oil Product			
	ibp-200°C	200-350	350-500	+500
Hydrotreated, no catalyst	3	81	16	0
HDS 1442A	12	85	3	0
HDS 3A	5	86	9	0
Reduced Mo (-100 mesh) + sulphur	6	88	5	1
Feedstock	4	84	11	1

Greenhills SRC

Data of Table 17 show addition of reduced molybdenum (-70 mesh) to Greenhills SRC had very little effect on the product slate compared to the test without catalyst. However, reduction in particle size of the catalyst, and the addition of sulphur, resulted in a considerable improvement in performance.

This improvement is shown by an increase in oil and asphaltene, and a decrease in the THF insoluble residue.

Greenhills conversion products under the uniform comparison conditions were:

	Product Distribution (wt.% daf)			
	Oil	Asphaltene	Preasphaltene	Residue
No catalyst	0.5	47.8	11.7	39.4
Sulphided HDS 1442A (CoMo)	6.3	61.9	9.1	21.9
Sulphided HDS 3A (NiMo)	2.6	69.4	8.4	18.8
Reduced Mo (-100 mesh)	2.0	53.8	12.5	30.9
Reduced Mo (-100 mesh) + S	7.4	71.7	8.2	11.4

The product distribution obtained with reduced molybdenum (-100 mesh) and sulphur was better than those which were obtained with the commercial catalysts or by thermal hydrotreatment. The addition of sulphur and catalyst seems to have enhanced the formation of asphaltene and reduced the formation of THF insoluble residue.

The presence of excess hydrogen sulphide has been shown to decrease the tendency of coke formation by acting as a hydrogen donor and stabilizing the radicals produced by pyrolysis (6-8). Hydrogen sulphide also increases the hydrocracking activity, and these factors together with the possible enhanced formation of molybdenum sulphide at lower levels of coking, could help to achieve this improvement in product distribution.

The hydrogen consumptions for tests using reduced molybdenum catalyst without sulphur were less than those obtained with the commercial catalysts (Tables 17 and 15). However, consumptions increased upon the addition of sulphur, corresponding to the enhanced product distribution.

Molybdenum was also added to Greenhills SRC in ammonia solution (see Table 17) in an equivalent concentration to the reduced molybdenum in order to investigate improved catalyst contact with the solvent refined coal. The product distribution was similar to that obtained with the -100 mesh reduced molybdenum, thus no further reduction in particle size of the prepared catalyst was considered.

Comparative TGA distillation data for the oil products were:

	Weight %			
	1bp-200°C	200-350°C	350-500°C	+500°C
Sulphided HDS 1442A (CoMo)	3	39	49	9
Sulphided HDS 3A (NiMo)	2	34	49	15
Reduced Mo (-100 mesh) +S	16	67	16	1

The boiling range distribution for the oils obtained by adding reduced molybdenum and sulphur was superior to those obtained with sulphided HDS 3A (NiMo) catalyst. The ibp-350°C fraction obtained from the reduced molybdenum catalyst with sulphur was much higher than those obtained with the other catalysts and feedstocks. This improvement in quality could be partially due to the hydrocracking ability of hydrogen sulphide (an intermediate product), and recent work (7) with lignite has shown that hydrogen sulphide enhanced the yield of both distillable and soluble oils. Further experiments would be required to confirm these results, but the interim conclusion is that reduced molybdenum plus sulphur has a useful catlytic effect in hydrotreating of highly asphaltic/preasphaltic feedstocks such as Greenhills SRC.

Devco SRC

The product distribution obtained by adding reduced molybdenum was similar to those with the commercial catalysts, but unlike the tests with Greenhills SRC, the addition of sulphur gave no improvement in product quality. The hydrogen requirements were higher for the tests with sulphur, but this was expected due to the production of hydrogen sulphide (Table 15 and 17).

The boiling ranges of the oils produced in these experiments were similar to each other and compared favourably with the results obtained with sulphided HDS 3A (NiMo) catalyst.

	Weight %			
	ibp-200°C	200-350°C	350-500°C	+500°C
Sulphided HDS 1442A (CoMo)	4	39	50	7
Sulphided HDS 3A (NiMo)	1	29	58	12
Reduced Mo (-100 mesh)	1	30	57	12
Reduced Mo (-100 mesh + S	1	26	59	14

Hat Creek SRC

The addition of reduced molybdenum, with and without sulphur, to Hat Creek SRC gave similar results (Table 17). Comparison of results with reduced molybdenum vs commercial catalysts (Tables 15 and 17) indicates that asphaltene yields were similar, but that the residues were greater with reduced molybdenum than those obtained with the commercial catalyst. Hydrogen consumptions for reduced molybdenum tests with and without sulphur were less than the values obtained with the commercial catalysts (Tables 15 and 17).

The boiling range distributions for the oils showed that the quality obtained by using commercial catalysts were better than those obtained with the reduced molybdenum catalyst. The amount of material boiling above 500°C was similar for all the tests with Hat Creek SRC.

	Weight %			
	ibp-200°C	200-350°C	350-500°C	+500°C
Sulphided HDS 1442A (CoMo)	19	60	19	2
Sulphided HDS 3A (NiMo)	5	57	34	4
Reduced Mo (-100 mesh)	1	41	53	5
Reduced Mo (-100 mesh) + S	3	41	49	7

Time (60 minutes) had very little effect with reduced molybdenum as compared with sulphided HDS 1442A (CoMo) catalyst. The oil yields increased with time resulting in slight changes in the asphaltenes and preasphaltenes. There was little residue formation during these prolonged reaction time experiments (Tables 17 and 19).

The boiling range distributions for these oils were not as favourable as those obtained with sulphided HDS 1442A (CoMo) catalyst, but time did improve the quality obtainable with reduced molybdenum and sulphur (Tables 18 and 20).

THERMOGRAVIMETRIC ANALYSES OF HYDROGENATION REACTION RESIDUES

The residues from hydrogenation experiments carried out at 425°C for 30 minutes were subjected to thermogravimentric analyses to determine their volatile matter, fixed carbon and ash contents. Similar determinations were carried out on the sulphided HDS 1442A (CoMo) and reduced molybdenum catalysts to allow for their presence in the residues. The results, calculated on a catalyst free basis, are shown in Table 21.

Comparison of results obtained with and without catalysts, especially for the coal derived liquids, showed that a decrease in volatile matter and fixed carbon content occurred for the residues with catalyst addition.

The values for fixed carbon content obtained with reduced molybdenum were always higher than for the commercial catalyst. This would seen to reflect the coking influence of the carbon used in the preparation of the reduced molybdenum catalyst.

The ash content of these residues increased after hydrotreatment with catalysts. The increase, which was usually greater for experiments using sulphided HDS 1442A (CoMo) catalyst, could have resulted from contamination (memory effect) by the walls of the tubing bomb and the metal balls used for mixing during the reaction. However, in addition to contamination, some of the increase may be due to the presence of organometallic compounds in the feedstock. These could possibly be precipitated by hydrogen sulphide or co-precipitated during coke formation.

COMPARISON OF REDUCED MOLYBDENUM AND MOLYBDENUM TRIOXIDE

Hydrotreatment of the feedstocks was carried out using molybdenum trioxide in equivalent molybdenum concentration to that used with reduced moylbdenum catalyst. Results (Table 22) indicate that product distributions obtained were similar to those obtained with reduced molybdenum except that the asphaltene contents were usually higher and the residues lower in the case of MoO_3.

Comparative data for Greenhills SRC with each catalyst (and none) are as follows:

	Hydrotreatment Products				
	Gas	Oil	Asphaltene	Preasphaltene	Residue
HDS 1442A	0.8	6.3	61.9	9.1	21.9
HDS 3A	0.8	2.6	69.4	8.4	18.8
Reduced Mo (-100 mesh)	0.8	2.0	53.8	12.5	30.9
Reduced Mo (-100 mesh)+S	1.3	7.4	71.7	8.2	11.4
MoO_3	0.6	0.4	62.7	11.9	24.4
Ammonium Molybdate + S	1.2	5.6	77.9	4.9	10.4
No catalyst	0.6	0.5	47.8	11.7	39.4
Feedstock	N/A	4.7	15.9	71.8	7.6

These results would seem to confirm that - in the absence of added sulphur - the carbon used to carbothermally reduce molybdenum trioxide tends to increase the residue for the feedstock derived from Greenhills coal.

These data also shows that sulphur is required with the unsupported Mo catalysts. When sulphur was present, comparable results were obtained for reduced Mo and ammonium molybdate. These tests also gave the lowest observed residue and preasphaltene products, while oil yields were comparable to the HDS 1442A supported CoMo catalysts.

FEEDSTOCK QUALITY VS TIME

Sequential extractions were carried out on the intial feedstocks at the begining and towards the end of the experimental program. There was little change shown in the component distribution for the feedstocks except for the asphaltene/preasphaltene distribution for the solvent refined coals (Table 23). The asphaltenes increased and the preasphaltenes decreased with time for these feedstocks. During the experimental program the bulk samples, which were stored at -10°C under nitrogen, were intermittently exposed to air. If oxidation occurred, then it is possible that the asphaltenes could increase as the oxygen containing compounds are usually concentrated in this fraction (3).

RECYCLE BEHAVIOUR OF SULPHIDED HDS-1442A (CoMo) AND REDUCED MOLYBDENUM CATALYSTS

Experiments were carried out using refinery pitch and Hat Creek SRC with sulphided HDS 1442A (CoMo) and reduced molybdenum catalysts. The residues from these experiments were used as catalysts for the subsequent experiments and this procedure was repeated through five cycles (Table 24).

Refinery Pitch

The effect shown by recycling reduced molybdenum and refinery pitch was small and resulted in a slight increase in oil yield and a decrease in asphaltene and residue. This improvement in product

quality with catalyst recycle would seem to indicate that recycling reduces the coking effect caused by the addition of carbon during the preparation of the reduced molybdenum catalyst, possibly due to accumulative effect of sulphur in the feedstock.

Hat Creek SRC

Recycle experiments using Hat Creek SRC with reduced molybdenum and sulphided HDS 1442A (CoMo) catalysts resulted in maximum oil yields during the third and fourth cycle respectively. The oil yield and quality (Table 25) was greater for the sulphided HDS 1442A (CoMo) catalyst, but the yield decreased to give a similar result to the reduced molybdenum for the fifth cycle.

The asphaltene content reached a maximum after the second cycle for both catalysts and then declined with further catalyst recycling. The decline in asphaltene yield was greater for the sulphided HDS 1442A (CoMo) than the reduced molybdenum catalyst and reflected the increase in oil yields discussed previously.

The preasphaltene yield was higher for experiments using reduced molybdenum. A maximum was reached on the third cycle, but then decreased with further processing. Recycling sulphided HDS 1442A (CoMo) catalyst resulted in a continuous increase in preasphaltenes yield from the third to the fifth cycle. The final preasphaltene yields for both catalysts were similar to each other.
This convergence of catalyst performance with recycling was further

confirmed by the THF insoluble residues and the hydrogen consumptions for these experiments. It would seem that sulphided HDS 1442A (CoMo) catalyst is more efficient initially, but its susceptibility to deactivation during recycling reduces the efficiency to a level equivalent to that obtained with reduced molybdenum. The efficiency of reduced molybdenum suffers initially because of enhanced coking, due to the presence of carbon used in the carbothermal reduction, but its performance improves with recycling. The final product distribution obtained after recycling was usually better than that obtained for the experiment without a catalyst.

CHARACTERIZATION OF THE CS_2 SOLUBLE PRODUCT AFTER HYDROTREATMENT

Ultimate analyses of CS_2 extracts after hydrotreatment (Table 26) were not directly comparable with those of initial feedstocks (Table 2), due to the presence of CS_2 insoluble material formed during the catalytic hydrotreatment. However, hydrogen contents increased and the nitrogen contents decreased after catalytic hydrogenation with the commercial and the reduced molybdenum catalysts.

Considering the the CS_2 extracts only (Table 26) it can be seen that the hydrogen contents were similar for experiments with HDS 3A (NiMo) and the reduced molybdenum catalysts. These values were greater than those obtained with sulpided HDS 1442A (CoMo) catalyst for the coal derived feedstocks.

The three catalysts tested were equally efficient in removing nitrogen from the selected feedstocks.

The boiling range of the CS_2 soluble fractions derived from the catalytic hydrogenation of selected feedstocks were determined by thermogravimetric analyses (Table 27). As discussed previously, these results cannot be compared directly with the initial feedstocks due to incomplete CS_2 extraction of the hydrogenated product. However, this error was small in the case of the refinery pitch.

Similar trends were shown by the coal derived liquids but the error due to insoluble material was greater. The gain in ibp-350°C fraction for the product derived from these feedstocks was independent of the catalyst used, with an exception in the case of sulphided HDS 1442A (CoMo) catalyst with Hat Creek SRC, which resulted in a greater ibp-350°C fraction of product. This trend was similar to that shown by the thermogravimetric analyses of the oils obtained from Hat Creek SRC as shown in Tables 16 and 18.

GENERAL EVALUATION OF TEST DATA

In general, results obtained in this program were disappointing in relation to the following parameters:

- insoluble residues
- oil formation
- hydrogen utilization

Insoluble residues produced in catalytic hydrogenation of SRC products were higher than expected in all cases, considering that the feedstocks were initially THF soluble. With reference to data of Table 23 (feedstock analyses vs age), it appears that - for the bituminous coal products - residue formation in untreated SRC occurred principally in the process of concentration from THF extract. Increases in residue formation during ~3 months storage (7.6 → 9.1% for Greenhills SRC, 6.3 → 7.4% for Devco SRC) were modest compared to changes (0 → 7.6% and 0 → 6.3%) in insolubles between THF extraction of the raw product and initial characterization. This suggests oxidation and/or polymerization occurred to a significant extent during initial handling.

Formation of hexane soluble "oils" from SRCs was low in all cases compared to - for example - 93% conversion of heptane insolubles cited by Shah et.al. (9) for severe catalytic hydrotreatment of SRC-1 of unstated origin. In the cited study, the SRC-1 product was diluted 1:1 with creosote oil (a coal tar distillate product) before hydrotreatment. This may be a significant factor since it is reasonable to expect on a simple mass action basis that polymerization/coking of SRC would be reduced by dilution with a compatible solvent. Besides the effect of dilution, phenols and nitrogen bases (eg. pyridine) in low boiling fractions (ie. < 208°) of coal liquids are known to enhance liquid yield in primary liquefaction. Thus, in retrospect, topping of the THF extract to 208° was probably a significant mistake. Topping to (about) 105°C to

remove THF and water, leaving one ring aromatics (xylenes, phenols, pyridines, etc.) would appear to have been a better procedure.

Observed hydrogen consumptions in the 1-1.5% range were clearly insufficient to even approach saturation of the aromatic (see Table 3) components of SRC feedstocks. The low change in hydrogen consumption between 30 and 60 minutes at 425°C for Greenhills and Devco SRCs (Tables 11 and 12) and the corresponding negligible decrease in residue suggests that reactive components of the feed have been either hydrogenated or coked to an unreactive condition during the first 30 minutes of treatment. Thus, with reference to the above discussion of high insoluble residues, the low hydrogen consumptions can be considered to be a related effect arising from removal of (potentially) hydrotreatable components by competing coke forming reaction.

INDICATED MODIFICATIONS TO THE TEST PROCEDURES

On the basis of the foregoing discussion, it appears that any further testwork should incorporate the following two modifications:

- conduct the primary product extraction and concentration operation under oxygen free conditions to minimize oxidation of SRC

- concentrate the primary (SRC) product only to the extent of light solvent and water removal, leaving diluting and potentially stabilizing components with the SRC feed to hydrotreatment.

CONCLUSIONS

GENERAL ASSESSMENT OF DATA

Observed low conversions and high residue formation indicate that hydrotreatment of the concentrated heavy (ie. SRC) fraction of liquefaction product may not be a viable procedure.

SPECIFIC EXPERIMENTAL CONCLUSIONS

1. The effect of increasing reaction temperature and time with catalyst addition was minimal for refinery pitch, but improved the product boiling range distribution in conversion of coal derived feedstocks.

2. The addition of catalysts seemed to prevent the degradation of oil to asphaltene for refinery pitch and anthracene oil, and asphaltene to preasphaltene for the remaining coal derived feedstocks.

3. Sulphided commercial catalysts HDS 1442A (CoMo) and HDS 3 A (NiMo) were more efficient than reduced molybdenum in preventing product degradation for refinery pitch and anthracene oil. However, providing coking could be reduced by sulphur addition in the case of Greenhills SRC, there was little difference in product distribution between these catalysts for the coal derived feedstocks.

4. The boiling range distributions for the oils were usually better for experiments using commercial catalysts, and the hydrogen consumptions for these experiments were always higher than experiments using reduced molybdenum.

5. Although the use of carbon is effective for reducing the molybdenum catalyst, its presence in the hydrogenation reaction of solvent refined coals seems to increase coke formation. The presence of excess sulphur prevents this in some instances but not in all.

   Comparison of results obtained with reduced molybdenum and molybdenum trioxide, indicates the presence of carbon in reduced molybdenum increases residue formation during hydrotreatment of feedstocks derived from coking coals.

6. Differences in catalyst performances on individual feedstocks were generally small, compared to large variations in yields from different feeds.

7. In the specific case of the Greenhills SRC, the catalyst combinations of reduced molybdenum plus sulphur, and molybdic oxide plus sulphur resulted in the lowest insoluble residues observed from this feedstock. For other feedstocks, the unsupported molybdenum catalysts were generally less effective than the commercial formulations tested.

8. Further experimentation under optimized conditions (see General Conclusion and General Assessment of Data) would be required to confirm that unsupported molybdenum has a useful advantage in treatment of the Greenhills (or similar) SRC feedstock.

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TABLE 1

ACTIVE CHEMICAL COMPOSITION* OF THE COMMERCIAL CATALYSTS

CATALYST	Active Components (wt%, dry basis)					
	MoO_3	CoO	NiO	Na_2O	Fe_2O_3	SO_4
Aero HDS-1442A (CoMo)	13.2	3.5	-	0.03	0.05	0.5
Aero HDS-3A (NiMo)	15.4	-	3.2	0.03	0.05	0.3

*Manufacturer's data; support is alumina for both catalysts

TABLE 2

PROXIMATE AND ULTIMATE ANALYSES OF INITIAL FEEDSTOCKS

FEEDSTOCK	Proximate Analyses (Weight %)				Ultimate Analyses (Weight % daf)				
	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	N	S	O
REFINERY PITCH	<0.1	93.4	6.6	<0.1	85.4	10.7	0.8	1.8	1.3
ANTHRACENE OIL	1.5	97.3	1.2	<0.1	90.2	5.6	0.8	0.8	2.7
GREENHILLS CDL *	2.3	45.2	52.5	<0.1	88.2	5.5	1.4	0.6	4.3
DEVCO CDL	1.3	54.5	44.1	0.2	87.5	5.6	1.9	0.6	4.4
HAT CREEK CDL	1.0	71.6	27.4	<0.1	84.9	6.0	1.1	0.6	7.4

* CDL = coal derived liquid

TABLE 3

^{1}HNMR ANALYSES OF INITIAL FEEDSTOCKS

FEEDSTOCK	$\frac{H_{ar}}{H_{ar} + H_{al} + H_o}$	$\frac{H_{al}}{H_{ar} + H_{al} + H_o}$	$\frac{H_o}{H_{ar} + H_{al} + H_o}$	$\frac{H_{ar}}{H_{al}}$
REFINERY PITCH	-	0.60	0.40	-
ANTHRACENE OIL	-	-	-	-
GREENHILLS CDL	0.40	0.47	0.13	0.84
DEVCO CDL	0.36	0.48	0.16	0.75
HAT CREEK CDL	0.39	0.53	0.08	0.74

Notation: aromatic protons: H_{ar}
aliphatic protons: H_{al}
olefinic protons: H_o
coal derived liquids: CDL

TABLE 4

BOILING RANGE OF INITIAL FEEDSTOCK AS DETERMINED BY THERMOGRAVIMETRIC ANALYSES

FEEDSTOCK	WEIGHT % DISTILLED			
	ibp - 200°C	200 - 350°C	350 - 500°C	+500°C
REFINERY PITCH	0	2	77	21
ANTHRACENE OIL	5	86	8	1
GREENHILLS CDL	3	3	20	74
DEVCO CDL	2	8	28	62
HAT CREEK CDL	2	22	34	42

TABLE 5

COMPOSITION OF INITIAL FEEDSTOCK AS DETERMINED BY SEQUENTIAL SOLVENT EXTRACTION

	PRODUCT DISTRIBUTION (wt.% daf)			
FEEDSTOCK	OIL	ASPHALTENE	PREASPHALTENE*	RESIDUE
REFINERY PITCH	93.3	6.7	0	0
ANTHRACENE OIL	89.8	5.8	3.3	1.1
GREENHILLS SRC	4.7	15.9	71.8	7.6
DEVCO SRC	6.0	15.3	72.4	6.3
HAT CREEK SRC	11.3	48.2	39.7	6.8

*Material soluble in pyridine

TABLE 6

EFFECT OF CATALYST PRESULPHIDING TEMPERATURE ON HYDROGENATION*
OF ANTHRACENE OIL

FEEDSTOCK	CATALYST PRESULPHIDING TEMPERATURE °C	PRODUCT DISTRIBUTION (wt.% daf)					
		GAS	OIL	ASPHALTENE	PREASPHALTENE	INSOLUBLE RESIDUE	HYDROGEN CONSUMPTION g/100g
FEEDSTOCK		N/A	89.8	5.8	3.3	1.1	N/A
ANTHRACENE OIL (NO CATALYST)	N/A	0.1	93.9	2.9	0	3.1	
ANTHRACENE OIL	400	0.04	96.3	1.4	0	2.2	1.21
ANTHRACENE OIL	300	0.05	97.9	1.3	0	0.7	1.31

*P1 = 6.8 MPa, Time = 30 minutes, Temperature = 400°C,
10 wt.% Sulphided HDS 1442A CoMo Catalyst

TABLE 7

HYDROGENATION* OF REFINERY PITCH USING SULPHIDED HDS 1442A (CoMo) CATALYST AT DIFFERENT TEMPERATURES AND TIMES

FEEDSTOCK (Conditions)	HYDROGENATION CONDITIONS		PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
	TEMPERATURE °C	TIME MINUTES	GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
REFINERY PITCH (UNTREATED)	-	-	-	93.3	6.7	0+	0	-
REFINERY PITCH (NO CATALYST)	425	30	0.7	78.4	20.0	0	0.9	0.03
REFINERY PITCH (CATALYST)	375	30	0.1	88.3	11.3	0.1	0.2	0.07
	400	30	0.1	88.2	10.6	0.2	0.9	0.25
	425	30	0.5	90.6	6.5	0	2.4	0.41
REFINERY PITCH (CATALYST)	425	15	0.3	83.7	15.2	0.3	0.5	0.38
	425	30	0.5	90.6	6.5	0	2.4	0.41
	425	60	1.0	87.8	8.9	0.7	1.6	0.62

*Pi = 6.8 MPa, 10 wt.% Sulphided Catalyst
+Pyridine Soluble

TABLE 8

BOILING RANGE OF OIL FRACTION FROM CATALYTICALLY HYDROGENATED* REFINERY PITCH AS DETERMINED BY THERMOGRAVIMETRIC ANALYSES

FEEDSTOCK (Conditions)	HYDROGENATION CONDITIONS		WEIGHT %			
	TEMPERATURE °C	TIME MINUTES	ibp - 200°C	200 - 350°C	350 - 500°C	+500°C
REFINERY PITCH (UNTREATED)	-	-	0	6	72	22
REFINERY PITCH (NO CATALYST)	425	30	3	16	64	17
REFINERY PITCH (CATALYST)	375	30	4	5	61	30
	400	30	4	6	65	25
	425	30	4	10	71	15
REFINERY PITCH (CATALYST)	425	15	1	5	67	27
	425	30	4	10	71	15
	425	60	2	12	66	20

*P1 = 6.8 MPa, 10 wt.% Sulphided HDS1422A (CoMo) Catalyst

TABLE 9

HYDROGENATION* OF ANTHRACENE OIL USING SULPHIDED HDS 1442A (CoMo) CATALYST AT DIFFERENT TEMPERATURES AND TIMES

FEEDSTOCK (Conditions)	HYDROGENATION CONDITIONS		PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
	TEMPERATURE °C	TIME MINUTES	GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
ANTHRACENE OIL (UNTREATED)	-	-	-	89.8	5.8	3.3+	1.1	-
ANTHRACENE OIL (NO CATALYST)	425	30	TRACE	88.1	10.5	0	1.4	0.07
ANTHRACENE OIL (CATALYST)	375	30	0.1	98.9	0.4	0	0.6	1.09
	400	30	0.1	97.9	1.3	0	0.7	1.31
	425	30	0.2	97.7	1.3	0	0.8	1.40
ANTHRACENE OIL (CATALYST)	425	15	0.1	98.9	0.3	0.1	0.6	1.25
	425	30	0.2	97.7	1.3	0	0.8	1.40
	425	60	0.3	97.8	0.3	0.5	1.1	1.54

*P1 = 6.8 MPa, 10 wt.% Sulphided Catalyst
+Pyridine Soluble

TABLE 10

BOILING RANGE OF OIL FRACTION FROM CATALYTICALLY HYDROGENATED* ANTHRACENE OIL AS DETERMINED BY THERMOGRAVIMETRIC ANALYSES

FEEDSTOCK (Conditions)	HYDROGENATION CONDITIONS		WEIGHT %			
	TEMPERATURE °C	TIME MINUTES	ibp - 200°C	200 - 350°C	350 - 500°C	+500°C
ANTHRACENE OIL (UNTREATED)	-	-	4	84	11	1
ANTHRACENE OIL (NO CATALYST)	425	30	3	81	16	0
ANTHRACENE OIL (CATALYST)	375	30	11	87	2	0
	400	30	12	85	3	0
	425	30	12	85	3	0
ANTHRACENE OIL (CATALYST)	425	15	6	88	6	0
	425	30	12	85	3	0
	425	60	5	86	7	2

*P1 = 6.8 MPa, 10 wt.% Sulphided HDS1422A (CoMo) Catalyst

TABLE 11

HYDROGENATION* OF GREENHILLS SRC USING SULPHIDED HDS 1442A (CoMo) CATALYST AT DIFFERENT TEMPERATURES AND TIMES

FEEDSTOCK (CONDITIONS)	HYDROGENATION CONDITIONS		PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
	TEMPERATURE °C	TIME MINUTES	GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
GREENHILLS SRC (UNTREATED)	-	-	-	3.5	38.8	25.8	31.8	-
GREENHILLS SRC (NO CATALYST)	400	30	0.1	2.5	42.0	22.0	33.4	0.06
	425	30	0.6	0.5	47.8	11.7	39.4	1.15
GREENHILLS SRC (CATALYST)	375	30	TRACE	2.4	54.9	12.0	30.7	0.32
	400	30	0.2	2.4	54.0	19.9	23.5	0.51
	425	30	0.8	6.3	61.9	9.1	21.9	0.89
GREENHILLS SRC (CATALYST)	425	15	0.5	2.6	53.7	11.7	31.5	0.64
	425	30	0.8	6.3	61.9	9.1	21.9	0.89
	425	60	1.5	2.9	65.9	9.9	19.8	1.1

*P1 = 6.8 MPa, 10 wt.% Sulphided Catalyst

TABLE 12

HYDROGENATION* OF DEVCO SRC USING SULPHIDED HDS 1442A (CoMo)) CATALYST AT DIFFERENT TEMPERATURES AND TIMES

FEEDSTOCK (CONDITIONS)	HYDROGENATION CONDITIONS		PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
	TEMPERATURE °C	TIME MINUTES	GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
DEVCO SRC (UNTREATED)	-	-	-	4.7	37.3	42.4	15.7	-
DEVCO SRC (NO CATALYST)	425	30	0.7	1.0	49.4	13.1	35.8	0.08
DEVCO SRC (CATALYST)	375	30	TRACE	2.0	70.0	9.6	18.4	0.39
	400	30	0.2	4.1	72.8	5.8	17.0	0.57
	425	30	0.7	3.1	69.1	10.4	16.7	0.84
DEVCO SRC (CATALYST)	425	15	0.5	1.7	60.5	9.6	27.8	0.58
	425	30	0.7	3.1	69.1	10.4	16.7	0.84
	425	60	1.3	1.6	74.4	6.3	16.4	1.20

*P1 = 6.8 MPa, 10 wt.% Sulphided Catalyst

TABLE 13

HYDROGENATION* OF HAT CREEK SRC USING SULPHIDED HDS 1442A (CoMo) CATALYST AT DIFFERENT TEMPERATURES AND TIMES

FEEDSTOCK (CONDITIONS)	HYDROGENATION CONDITIONS		PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
	TEMPERATURE °C	TIME MINUTES	GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
HAT CREEK SRC (UNTREATED)	-	-	-	5.0	60.1	30.3	4.7	-
HAT CREEK SRC (NO CATALYST)	425	30	1.3	1.5	51.0	7.3	30.7	0.14
HAT CREEK SRC (CATALYST)	375	30	0.2	3.5	76.8	5.7	6.4	0.78
	400	30	0.4	4.6	77.3	3.5	6.0	1.07
	425	30	0.9	9.1	69.2	4.7	7.7	1.40
HAT CREEK SRC (CATALYST)	425	15	0.7	2.5	73.8	5.7	7.2	1.14
	425	30	0.9	9.1	69.2	4.7	7.7	1.40
	425	60	1.3	15.7	62.6	2.6	5.8	1.64

*P1 = 6.8 MPa, 10 wt.% Sulphided Catalyst

TABLE 14

BOILING RANGE OF OIL FRACTION FROM CATALYTICALLY HYDROGENATED* HAT CREEK SRC AS DETERMINED BY THERMOGRAVIMETRIC ANALYSES

FEEDSTOCK (CONDITIONS)	HYDROGENATION CONDITIONS		WEIGHT %			
	TEMPERATURE °C	TIME MINUTES	ibp - 200°C	200 - 350°C	350 - 500°C	+500°C
HAT CREEK SRC (NO CATALYST)	425	30	9	53	34	4
HAT CREEK SRC (CATALYST)	425	15	5	54	39	2
	425	30	19	60	19	2
	425	60	22	63	13	2

*P1 = 6.8 MPa, 10 wt.% Sulphided HDS1422A (CoMo) Catalyst

TABLE 15

HYDROGENATION* OF INITIAL FEEDSTOCKS WITH COMMERCIAL CATALYSTS

FEEDSTOCK	CATALYST	PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
		GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
REFINERY PITCH	No Catalyst	0.7	78.4	20.0	0	0.9	0.03
	Sulphided HDS 1442A (CoMo)	0.5	90.6	6.5	0	2.2	0.41
	Sulphided HDS 3A (NiMo)	0.1	86.6	9.8	0.1	3.4	0.43
ANTHRACENE OIL	No Catalyst	TRACE	88.1	10.5	0	1.4	0.07
	Sulphided HDS 1442A (CoMo)	0.2	97.7	1.3	0	0.8	1.40
	Sulphided HDS 3A (NiMo)	0.1	96.0	0.8	0	3.1	1.81
GREENHILLS SRC	No Catalyst	0.6	0.5	47.8	11.7	39.4	1.15
	Sulphided HDS 1442A (CoMo)	0.8	6.3	61.9	9.1	21.9	0.89
	Sulphided HDS 3A (NiMo)	0.8	2.6	69.4	8.4	18.8	0.92
DEVCO SRC	No Catalyst	0.7	1.0	49.4	13.1	35.8	0.08
	Sulphided HDS 1442A (CoMo)	0.7	3.1	69.1	10.4	16.7	0.84
	Sulphided HDS 3A (NiMo)	0.8	2.1	66.6	9.6	20.9	0.91
HAT CREEK SRC	No Catalyst	1.3	1.5	51.0	7.3	30.7	0.14
	Sulphided HDS 1442A (CoMo)	0.9	9.1	69.2	4.7	7.7	1.40
	Sulphided HDS 3A (NiMo)	1.0	2.5	70.7	6.8	6.9	1.48

*P1 = 6.8 MPa, Time = 30 minutes, Temperature = 425°C,
10 wt.% Sulphided Catalyst

TABLE 16

BOILING RANGE OF OIL FRACTION FROM CATALYTICALLY HYDROGENATED* FEEDSTOCKS AS DETERMINED BY THERMOGRAVIMETRIC ANALYSES

FEEDSTOCK	CATALYST	WEIGHT %			
		ibp - 200°C	200 - 350°C	350 - 500°C	+500°C
REFINERY PITCH	No Catalyst	3	16	64	17
	Sulphided HDS 1442A (CoMo)	4	10	71	15
	Sulphided HDS 3A (NiMo)	0	7	65	28
ANTHRACENE OIL	No Catalyst	3	81	16	0
	Sulphided HDS 1442A (CoMo)	12	85	3	0
	Sulphided HDS 3A (NiMo)	5	86	9	0
GREENHILLS SRC	No Catalyst	N.D.	N.D.	N.D.	N.D.
	Sulphided HDS 1442A (CoMo)	3	39	49	9
	Sulphided HDS 3A (NiMo)	2	34	49	15
DEVCO SRC	No Catalyst	8	40	41	11
	Sulphided HDS 1442A (CoMo)	4	39	50	7
	Sulphided HDS 3A (NiMo)	1	29	58	12
HAT CREEK SRC	No Catalyst	9	53	34	4
	Sulphided HDS 1442A (CoMo)	19	60	19	2
	Sulphided HDS 3A (NiMo)	5	57	34	4

N.D. = not determined (insufficient sample)
*P1 = 6.8 MPa, Time = 30 minutes, Temperature = 425°C,
10 wt.% Sulphided Catalyst

TABLE 17

HYDROGENATION* OF INITIAL FEEDSTOCKS WITH REDUCED MOLYBDENUM CATALYST

FEEDSTOCK	CATALYST	PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
		GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
REFINERY PITCH	No Catalyst	0.7	78.4	20.0	0	0.9	0.03
	Reduced Mo (-70 Mesh)	0.5	80.4	12.7	0	6.4	0.37
	Reduced Mo (-100 Mesh)	0.5	80.6	13.0	0	5.9	0.33
	Reduced Mo (-100 Mesh)+S	0.6	78.5	12.3	0	8.6	0.33
ANTHRACENE OIL	No Catalyst	TRACE	88.1	10.5	0	1.4	0.07
	Reduced Mo (-70 Mesh)	0.1	93.9	0.9	0	5.1	0.83
	Reduced Mo (-100 Mesh)	0.1	95.2	0.7	0	4.0	0.81
	Reduced Mo (-100 Mesh)+S	0.2	90.0	3.5	0	6.3	0.89
GREENHILLS SRC	No Catalyst	0.6	0.5	47.8	11.7	39.4	1.15
	Reduced Mo (-70 Mesh)	0.8	1.0	47.7	9.7	40.8	0.40
	Reduced Mo (-70 Mesh)+S	0.9	1.5	55.6	10.0	32.0	0.66
	Reduced Mo (-100 Mesh)	0.8	2.0	53.8	12.5	30.9	0.50
	Reduced Mo (-100 Mesh)+S	1.3	7.4	71.7	8.2	11.4	1.31
	MoO_3+NH_4OH+S	1.2	5.6	77.9	4.9	10.4	1.25
DEVCO SRC	No Catalyst	0.7	1.0	49.4	13.1	35.8	0.08
	Reduced Mo (-100 Mesh)	0.8	1.1	67.8	9.0	21.3	0.63
	Reduced Mo (-100 Mesh)+S	0.8	1.1	64.3	9.6	24.2	1.19
HAT CREEK SRC	No Catalyst	1.3	1.5	51.0	7.3	30.7	0.14
	Reduced Mo (-100 Mesh)	1.4	1.0	71.3	8.0	10.3	0.95
	Reduced Mo (-100 Mesh)+S	1.8	1.5	71.8	2.1	12.6	0.74

*P1 = 6.8 MPa, Time = 30 minutes, Temperature = 425°C,
Mo concentration = Mo content in 10 wt.% HDS 1442A (CoMo)

TABLE 18

BOILING RANGE OF OIL FRACTION FROM CATALYTICALLY HYDROGENATED* FEEDSTOCKS AS DETERMINED BY THERMOGRAVIMETRIC ANALYSES

FEEDSTOCK	CATALYST	WEIGHT %			
		ibp - 200°C	200 - 350°C	350 - 500°C	+500°C
REFINERY PITCH	No Catalyst	3	16	64	17
	Reduced Mo (-70 Mesh)	1	7	60	32
	Reduced Mo (-100 Mesh)	0	7	65	28
	Reduced Mo (-100 Mesh)+S	1	8	67	24
ANTHRACENE OIL	No Catalyst	3	81	16	0
	Reduced Mo (-70 Mesh)	4	88	8	0
	Reduced Mo (-100 Mesh)	3	86	11	0
	Reduced Mo (-100 Mesh)+S	6	88	5	1
GREENHILLS SRC	No Catalyst	N.D.	N.D.	N.D.	N.D.
	Reduced Mo (-70 Mesh)+S	18	48	29	5
	Reduced Mo (-100 Mesh)+S	16	67	16	1
	MoO_3+NH_4OH+S	2	52	40	6
DEVCO SRC	No Catalyst	8	40	41	11
	Reduced Mo (-100 Mesh)	1	30	57	12
	Reduced Mo (-100 Mesh)+S	1	26	59	14
HAT CREEK SRC	No Catalyst	9	53	34	4
	Reduced Mo (-100 Mesh)	1	41	53	5
	Reduced Mo (-100 Mesh)+S	3	41	49	7

N.D. = not determined (insufficient sample)
*Pi = 6.8 MPa, Time = 30 minutes, Temperature = 425°C,
Mo concentration ≡ Mo Content
in 10 wt % HDS 1442A (CoMo)

TABLE 19

HYDROGENATION* OF HAT CREEK SRC USING REDUCED MOLYBDENUM CATALYST AT LONG REACTION TIMES

FEEDSTOCK	CATALYST	PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
		GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
HAT CREEK SRC	No Catalyst	1.9	1.0	61.7	10.7	20.7	0.37
	Sulphided HDS 1443A (CoMo)	1.3	15.7	62.6	2.6	5.8	1.64
	Reduced Mo (-100 Mesh)	2.2	2.2	71.7	4.1	11.2	1.35
	Reduced Mo (-100 Mesh)+S	1.9	4.8	67.7	2.6	14.7	1.50

*P1 = 6.8 MPa, Temperature = 425°C, Time = 60 Minutes, 10 wt.% Sulphided HDS 1442A (CoMo)
Mo Concentration = Mo content in 10wt.% HDS 1442A (CoMo)

TABLE 20

BOILING RANGE OF OIL FRACTION FROM CATALYTICALLY HYDROGENATED* HAT CREEK SRC AS DETERMINED BY THERMOGRAVIMETRIC ANALYSES

FEEDSTOCK	CATALYST	WEIGHT %			
		ibp - 200°C	200 - 350°C	350 - 500°C	+500°C
HAT CREEK SRC	No Catalyst	3	49	40	8
	Sulphided HDS 1442A (CoMo)	22	63	13	2
	Reduced Mo (-100 Mesh)	1	41	52	6
	Reduced Mo (-100 Mesh)+S	11	60	26	3

*Pi = 6.8 MPa, Time = 30 minutes, Temperature = 425°C,
Mo concentration = Mo content in 10 wt.% HDS 1442A (CoMo)

TABLE 21

THERMOGRAVIMETRIC ANALYSES OF HYDROGENATION REACTION* RESIDUES

FEEDSTOCK	CATALYST	PRODUCT WEIGHT (g) CATALYST FREE BASIS			
		RESIDUE	VOLATILE MATTER	FIXED CARBON	ASH
REFINERY PITCH	No Catalyst	N.D.**	N.D.	N.D.	N.D.
	Sulphided HDS 1442A (CoMo)	0.55	0.20	0.13	0.22
	Reduced Mo (-100 Mesh)	1.29	0.22	0.99	0.08
ANTHRACENE OIL	No Catalyst	0.28	0.05	0.18	0.05
	Sulphided HDS 1442A (CoMo)	0.25	0.08	NIL	0.17
	Reduced Mo (-100 Mesh)	0.87	0.26	0.40	0.21
GREENHILLS SRC	No Catalyst	7.68	2.56	5.01	0.10
	Sulphided HDS 1442A (CoMo)	4.30	2.46	1.62	0.22
	Reduced Mo (-100 Mesh)	6.13	0.91	5.19	0.03
DEVCO SRC	No Catalyst	7.09	1.35	5.67	0.05
	Sulphided HDS 1442A (CoMo)	3.31	0.65	2.57	0.09
	Reduced Mo (-100 Mesh)	4.28	0.62	3.48	0.18
HAT CREEK SRC	No Catalyst	6.08	1.62	4.31	0.14
	Sulphided HDS 1442A (CoMo)	1.54	0.33	0.87	0.34
	Reduced Mo (-100 Mesh)	2.13	0.29	1.67	0.17

* P1 = 6.8 MPa, Temperature = 425°C, Time = 30 minutes, 10 wt.% Sulphided HDS 1442A (CoMo), Mo Concentration, Mo content in 10 wt.% HDS 1442A

** N.D. = Not Determined

TABLE 22

COMPARISON OF REDUCED MOLYBDENUM AND MOLYBDENUM TRIOXIDE

FEEDSTOCK	CATALYST	PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g MATERIAL
		GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
REFINERY PITCH	Reduced Mo (-100 Mesh)	0.5	80.6	13.0	0	5.9	0.33
	MoO_3	0.4	82.9	16.1	0	0.5	0.34
ANTHRACENE OIL	Reduced Mo (-100 Mesh)	0.1	95.2	0.7	0	4.0	0.81
	MoO_3	0.1	94.1	5.1	0	0.8	0.52
GREENHILLS SRC	Reduced Mo (-100 Mesh)	0.8	2.0	53.8	12.5	30.9	0.50
	MoO_3	0.6	0.4	62.7	11.9	24.4	0.66
DEVCO SRC	Reduced Mo (-100 Mesh)	0.8	1.1	67.8	9.0	21.3	0.63
	MoO_3	0.7	0.5	70.2	10.8	17.9	0.63
HAT CREEK SRC	Reduced Mo (-100 Mesh)	1.4	1.0	71.3	8.0	10.3	0.95
	MoO_3	1.1	2.0	76.9	5.8	9.9	0.92

*P1 = 6.8 MPa, Time = 30 minutes, Temperature = 425°C,
Mo concentration = Mo content in 10 wt.% HDS 1442A (CoMo)

TABLE 23

COMPARISON OF PRODUCT DISTRIBUTION OF FEEDSTOCK WITH TIME

FEEDSTOCK	DATE	PRODUCT DISTRIBUTION (wt.% daf)			
		OIL	ASPHALTENE	PREASPHALTENE*	RESIDUE
REFINERY PITCH	July 82	93.3	6.7	NIL	NIL
	Sept 82	95.4	4.6	NIL	NIL
ANTHRACENE OIL	July 82	89.8	5.8	3.3	1.1
	Sept 82	98.9	0.6	NIL	0.5
GREENHILLS SRC	July 82	4.7	15.9	71.8	7.6
	Sept 82	3.7	36.7	50.5	9.1
DEVCO SRC	July 82	6.0	15.3	72.4	6.3
	Sept 82	4.3	31.9	56.4	7.4
HAT CREEK SRC	July 82	11.3	48.2	39.7	0.8
	Sept 82	8.6	57.0	34.0	0.4

*MATERIAL SOLUBLE IN PYRIDINE

TABLE 24

COMPARISON OF RECYCLE BEHAVIOUR OF SULPHIDED HDS-1442A (CoMo) AND REDUCED MOLYBDENUM CATALYSTS

FEEDSTOCK	CATALYST	CYCLE	PRODUCT DISTRIBUTION (wt.% daf)					HYDROGEN CONSUMPTION g/100g FEEDSTOCK
			GAS	OIL	ASPHALTENE	PREASPHALTENE (THF SOLUBLE)	RESIDUE	
REFINERY PITCH	None	-	0.7	78.4	20.0	0	0.9	0.03
	Reduced Mo (-100 Mesh)	1	0.5	80.6	13.4	0	5.6	0.25
		2	0.4	81.4	16.8	0	1.5	0.32
		3	1.5	80.9	16.3	0	1.4	0.38
		4	0.5	-	-	0	1.0	0.32
		5	0.5	83.7	14.9	0	0.9	0.34
HAT CREEK SRC	None	-	1.3	1.5	51.0	7.3	30.7	0.14
	Reduced Mo (-100 Mesh)	1	1.3	3.0	72.8	5.7	10.6	1.12
		2	1.5	1.5	82.0	5.0	4.4	1.10
		3	1.4	5.6	78.4	10.5	6.6	1.15
		4	1.5	1.5	80.4	10.7	2.1	1.20
		5	1.4	2.0	78.4	8.9	4.7	1.23
HAT CREEK SRC	None	-	1.3	1.5	51.0	7.3	30.7	0.14
	Sulphided HDS 1442A (CoMo)	1	1.0	4.6	71.8	3.8	6.6	1.44
		2	0.3	4.6	79.8	4.5	3.2	1.26
		3	0.9	9.2	74.4	3.0	3.1	1.29
		4	1.1	15.2	67.3	6.7	5.7	1.27
		5	1.1	3.5	72.8	7.0	7.0	1.22

P_i = 6.8 MPa; Temperature = 425°C; Time = 30 minutes; 10 wt.% Sulphided HDS-1442A (CoMo), Mo = Mo content in 10 wt.% HDS-1442A (CoMo)

TABLE 25

BOILING RANGE OF OIL FRACTION OBTAINED FROM RECYCLING SELECTED CATALYSTS AS DETERMINED BY THERMOGRAVIMETRIC ANALYSES

FEEDSTOCK	CATALYST	CYCLE	WEIGHT %			
			1bp - 200°C	200 - 350°C	350 - 500°C	+500°C
HAT CREEK SRC	Feedstock	-	9	53	34	4
	Reduced Mo (-100 Mesh)	1	8	60	28	4
		2	4	49	40	7
		3	24	57	16	3
		4	5	50	40	5
		5	3	46	45	6
HAT CREEK SRC	Feedstock	-	9	53	34	4
	Sulphided HDS 1442A (CoMo)	1	10	68	19	3
		2	25	57	15	3
		3	18	63	17	2
		4	37	54	7	2
		5	35	53	8	4

Pi = 6.8 MPa, Temperature = 425°C, Time = 30 minutes
10 wt.% Sulphided HDS 1442A (CoMo) Catalyst
Mo = Mo Content in 10 wt.% HDS 1442A (CoMo)

TABLE 26

COMPARISON OF ULTIMATE ANALYSES OF CS_2 SOLUBLE MATERIAL
AFTER CATALYTIC HYDROGENATION*

FEEDSTOCK	CATALYST	ULTIMATE ANALYSES wt.%				
		C	H	N	S	O
REFINERY PITCH	Sulphided HDS 1442A (CoMo)	86.5	11.3	0.7	N.D.	N.D.
	Reduced Mo (-100 Mesh)	86.7	11.3	0.7	N.D.	N.D.
DEVCO SRC	Sulphided HDS 1442A (CoMo)	87.0	6.4	1.6	N.D.	N.D.
	Sulphided HDS 3A (NiMo)	87.3	6.6	1.6	N.D.	N.D.
	Reduced Mo (-100 Mesh)	86.7	6.6	1.6	N.D.	N.D.
HAT CREEK SRC	Sulphided HDS 1442A (CoMo)	87.2	6.6	0.9	-	3.2
	Sulphided HDS 3A (NiMo)	87.2	7.1	1.0	N.D.	N.D.
	Reduced Mo (-100 Mesh)	87.4	7.0	0.9	-	4.3

*P1 = 6.8 MPa, Temperature = 425°C, Time = 30 minutes, 10 wt.% Sulphided Catalyst
Mo Conentration = Mo Content in 10 wt.% HDS 1442A (CoMo)
N.D. - Not Done

TABLE 27

COMPARISON OF BOILING RANGE OF CS_2 SOLUBLE MATERIAL AFTER CATALYTIC HYDROGENATION*

FEEDSTOCK	CATALYST	WEIGHT %			
		ibp - 200°C	200 - 350°C	350 - 500°C	+500°C
REFINERY PITCH	No Catalyst	0	2	77	21
	Sulphided HDS 1442A (CoMo)	1	7	71	21
	Reduced Mo (-100 Mesh)	2	9	71	18
DEVCO SRC	No Catalyst	2	8	28	62
	Sulphided HDS 1442A (CoMo)	5	20	29	46
	Sulphided HDS 3A (NiMo)	4	20	29	47
	Reduced Mo (-100 Mesh)	4	18	32	46
HAT CREEK SRC	No Catalyst	2	20	34	44
	Sulphided HDS 1442A (CoMo)	13	31	28	28
	Sulphided HDS 3A (NiMo)	8	30	32	30
	Reduced Mo (-100 Mesh)	7	31	34	28

*P1 = 6.8 MPa, Temperature = 425°C, Time = 30 minutes, 10 wt.% Sulphided Catalyst
Mo Concentration - Mo Content in 10 wt.% HDS 1442A (CoMo)

FIGURE I

SCHEMATIC DIAGRAM OF TUBING BOMB REACTOR